362
637-A
I28.23: 9021

RI 9021

Bureau of Mines Report of Investigations/1986

ORIGINAL
COMPLETED
15.

Flocculation and Dewatering of Montmorillonite Modified by Ion Exchange

By D. A. Stanley and B. J. Scheiner

UNITED STATES DEPARTMENT OF THE INTERIOR

BEST COPY AVAILABLE

Report of Investigations 9021

Flocculation and Dewatering of Montmorillonite Modified by Ion Exchange

By D. A. Stanley and B. J. Scheiner

UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
Robert C. Horton, Director

This report is based upon work done under an agreement between the University of Alabama and the Bureau of Mines.

BEST COPY AVAILABLE

Library of Congress Cataloging in Publication Data:

Stanley, D. A. (Donald A.)

Flocculation and dewatering of montmorillonite modified by ion exchange.

(Report of investigations / Bureau of Mines ; 9021)

Bibliography: p. 10.

Supt. of Docs. no.: I 28.23: 9021.

1. Clay wastes–Dewatering. 2. Hydrometallurgy–Waste disposal. 3. Montmorillonite. 4. Flocculation. 5. Ion exchange. 6. Polyethylene oxide. I. Scheiner, Bernard J. II. Title. III. Series: Report of investigations (United States. Bureau of Mines) ; 9021.

TN23.U43 [TD899.M43] 622s [669'.028'3] 85-600360

BEST COPY AVAILABLE

CONTENTS

	Page
Abstract	1
Introduction	2
Experimental work	2
Materials	2
Method	2
Results	3
Treatment of the data	3
Flocculation and dewatering of phosphatic clay waste and montmorillonite clays	3
Empirical parameters and ionic radii	4
Relationship between n and the hydrated radii	5
Relationship between k and the unhydrated ionic radii	5
Relationship of the solids content to the ionic radii	6
Electron photomicrographs	9
Discussion and conclusions	9
References	10

ILLUSTRATIONS

1.	Plot for determination of the parameters of equation 1	3
2.	Plot for calculation of equation 1 parameters from the data of table 1	4
3.	Relation between n and c/H_e	5
4.	Plot of $k^{1/n}$ versus R^2/c	6
5.	Plots of A and R/c	6
6.	Plot of observed percent solids data versus one-factor reproduced data	6
7.	Relation between A and percent solids for data reproduced from one-factor statistical analysis	7
8.	Plots of reciprocal of percent solids versus R/c	7
9.	Photomicrograph of Na-exchanged montmorillonite dewatered by PEO	8
10.	Photomicrograph of Ba-exchanged montmorillonite dewatered by PEO	8

TABLES

1.	PEO requirement for flocculating and dewatering phosphate clay waste	4
2.	Empirical parameters for the dewatered clays	5
3.	PEO required to dewater the ion-exchanged clays	5
4.	Ionic radii of the exchanged ions	5
5.	Measured solids content and one-factor reproduced solids content	7

BEST COPY AVAILABLE

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	ml.	milliliter
g	gram	pct	percent
g/kg	gram per kilogram	r/min	revolution per minute
in	inch	wt pct	weight percent
L	liter		

BEST COPY AVAILABLE

FLOCCULATION AND DEWATERING OF MONTMORILLONITE MODIFIED BY ION EXCHANGE

By D. A. Stanley [1] and B. J. Scheiner [2]

ABSTRACT

The Bureau of Mines is investigating a method of dewatering flocculated fine-particle waste that involves treating the waste with a high-molecular-weight polymer such as polyethylene oxide (PEO) followed by dewatering on a static screen and/or in a trommel.

Dilution of the polymer solution used for dewatering and use of the ion-exchanged form of the montmorillonite clay were found to be major factors determining the amount of polymer required to dewater clay-containing slurries. The amount of polymer, A, required to dewater ion-exchanged montmorillonite can be described by the equation,

$$A^n = kC + b$$

where n, k, and b are empirical constants and C is the concentration of the polymer solution used for dewatering. Clays that require large amounts of polymer for dewatering also dewater to a lower solids content.

The concentration of the polymer solution is important because it affects the radius of the polymer coil in solution and hence its ease of transfer to a bridging configuration by shear. The constant, n, a function of the charge to hydrated radius of the exchange ion, relates to the strength of the bond between the polymer and the surface of the clay through a water bridge. The constant k is related to the hydrated radius for sodium or to the unhydrated radius for the other exchange ions.

[1]Supervisory research chemist.
[2]Supervisory metallurgist.
Tuscaloosa Research Center, Bureau of Mines, Tuscaloosa, AL.

BEST COPY AVAILABLE

INTRODUCTION

For several years the Bureau of Mines has been investigating a system for dewatering fine-particle waste generated during the processing of ores and concentrates. This system is based on flocculation by a high-molecular-weight polymer followed by mechanical dewatering induced by passage of the flocculated waste over a static screen and/or through a trommel. The method has been field-tested for the dewatering of phosphatic clay waste and coal-clay waste (1-2).[3]

Previous dewatering studies showed that calcium ion exchange of montmorillonite-containing phosphate slimes reduced the amount of PEO needed for dewatering (3). It was also determined that the concentration of the PEO solution added to the phosphatic clay waste affected the amount of PEO required for successful dewatering (4). An empirical relationship was discovered for attapulgite clays that related the amount of polymer used for dewatering to the ion-exchange form of the clay and to the polymer concentration (5). This investigation extends the application of the empirical equation to the dewatering of ion-exchanged montmorillonite clay and to phosphatic clay waste containing ion-exchanged montmorillonite.

EXPERIMENTAL WORK

MATERIALS

The six phosphatic clay waste samples used in this study were collected at several phosphate mines in Florida. The principal minerals in these samples, as identified by X-ray diffraction, were montmorillonite, apatite, and quartz. The ion-exchanged montmorillonite used in this study was prepared from Wyoming bentonite. The montmorillonite was ion-exchanged by mixing 200 g clay with 2 L distilled water and 200 mL of a solution (1N) of the appropriate metal chloride. The montmorillonite clay suspension was allowed to settle overnight, and the supernate was removed. The sediment was resuspended in 4 L distilled water and again allowed to settle overnight. This washing procedure was repeated eight times. The clay slurry was stored in plastic containers until used. A commercially available PEO with a molecular weight of 8 million was used in all flocculation experiments.

METHOD

Dewatering experiments were conducted by placing 200 mL clay slurry in a 250-mL beaker. The slurry in the beaker was stirred at 500 r/min with a Teflon-coated[4] magnetic stir bar 1.25 to 1.5 in long. Approximately 1 drop per second of PEO solution was added to the slurry until the endpoint was reached. This endpoint is characterized by large aggregates of flocs, a minimum floc volume, and a change from individual floc movement to rotation of the entire slurry mass in the beaker. The supernate was clear rather than turbid at the endpoint.

When the endpoint was reached, the solids were removed from the beaker and hand-squeezed to remove additional water. Hand squeezing was employed to simulate the action of the static screen and trommel and is repeatable within an experimental error of ±5 pct. The dewatered clay was weighed, dried overnight at 105° C, and reweighed, and the solids content was calculated from the two weights.

---

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

[4]Reference to specific products does not imply endorsement by the Bureau of Mines.

BEST COPY AVAILABLE

RESULTS

TREATMENT OF THE DATA

In previous studies, an empirical equation was developed that predicted the amount of polymer required to dewater attapulgite clays (5). The equation is

$$A^n = kC + b, \qquad (1)$$

where A is the amount of polymer (PEO) required in grams per kilograms of clay solids; n, k, and b are empirical constants; and C is the concentration, in weight percent, of the polymer solution used for dewatering. To determine if equation 1 is applicable to waste containing montmorillonite clays, a sample of phosphate clay waste with a high content of montmorillonite was dewatered and the empirical constants were determined.

The basis of this method is illustrated in figure 1, which is a plot of the amount of polymer, A, raised to several different powers, n, versus the concentration, C, of the polymer solution. For this initial test a phosphate clay waste slurry, sample 6, was used. For a selected value of 1.72 for n, the points lie on a straight line with an intercept, b, of 0.031 and a slope, k, of 19.93.

FLOCCULATION AND DEWATERING OF PHOSPHATIC CLAY WASTE AND MONTMORILLONITE CLAYS

The amount of PEO solution required to dewater six phosphatic clay wastes from Florida at different PEO solution concentrations is shown in table 1.

By using equation 1 and data from table 1, the empirical parameters, k, n, and b, were calculated; these are shown in table 2. The method described above was used, in which the amount of PEO was plotted against the PEO concentration for several different values of n. Figure 2 shows the straight lines obtained when the proper value of n is chosen.

This procedure was repeated for Na^+, K^+, Mg^{++}, Ca^{++}, and Al^{+++} ion-exchanged montmorillonite, and the results of the dewatering experiments appear in table 3.

Using the constants from table 2 for the ion-exchanged montmorillonite and equation 1, the amount of PEO required, A, to dewater the samples was calculated and was included in table 3 for comparison with the results obtained experimentally. The results show that there is a good correlation between the observed values of A and the calculated values obtained by using equation 1 for all ions except the sodium ion. The sodium ion-exchanged clay forms a gellike structure for which it is very difficult to determine the endpoint. This indicates that equation 1 is a good representation of the flocculation process for montmorillonite-containing clays and PEO.

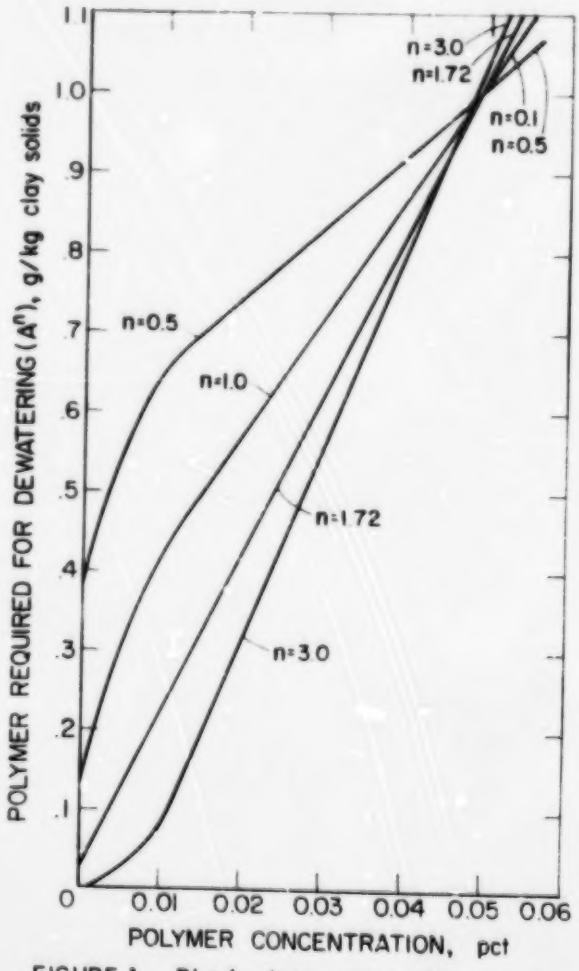

FIGURE 1. - Plot for determination of the parameters of equation 1.

BEST COPY AVAILABLE

TABLE 1. - PEO requirement for flocculating and dewatering phosphate clay waste

PEO conc, wt pct	Method[1]	PEO dosage, g/kg solids					
		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
0.25	Exp.	1.21	0.66	0.35	NAp	NAp	NAp
.25	Calc.	1.21	.66	.35	NAp	NAp	NAp
.10	Exp.	.80	.42	.28	NAp	NAp	NAp
.10	Calc.	.80	.43	.28	NAp	NAp	NAp
.05	Exp.	.57	.33	.24	3.38	1.59	1.02
.05	Calc.	.60	.33	.24	3.37	1.59	1.02
.010	Exp.	.44	.25	.19	1.14	.62	.43
.010	Calc.	.37	.24	.19	1.13	.60	.43
.005	Exp.	.28	.22	.19	.64	.25	.31
.005	Calc.	.32	.22	.17	.68	.36	.31
.0025	Exp.	NAp	NAp	NAp	.29	.15	.23
.0025	Calc.	NAp	NAp	NAp	.37	.16	.23
.001	Exp.	NAp	NAp	NAp	.24	.10	.18
.001	Calc.	NAp	NAp	NAp	.09	ND	.18

NAp Not applicable.
[1]Exp. = experimental; Calc. = calculated.

EMPIRICAL PARAMETERS AND IONIC RADII

Several relationships between the parameters of equation 1 and the hydrated (H_R) and unhydrated (R) ionic radii of the exchange ions of montmorillonite were found, and these relationships provide insight into the mechanism of clay dewatering with PEO. The ionic radii used were taken from Nightingale (6) and are listed in table 4.

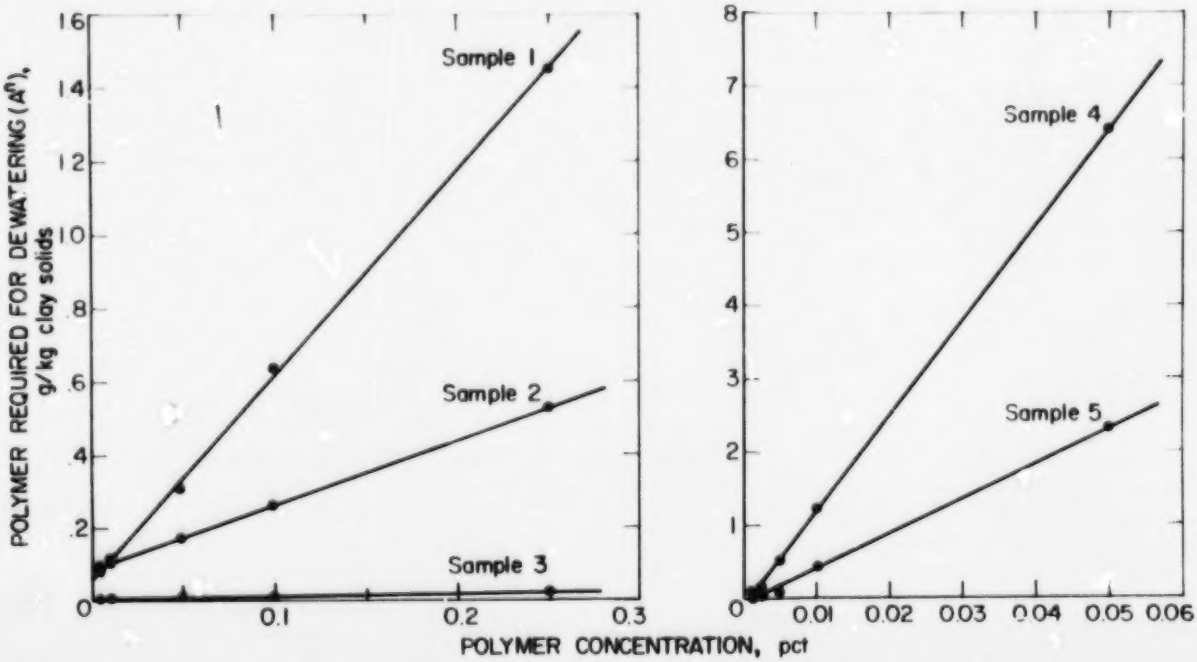

FIGURE 2. - Plot for calculation of equation 1 parameters from the data of table 1.

BEST COPY AVAILABLE

TABLE 2. - Empirical parameters for the dewatered clays

Sample	Constant		
	Slope, k	Exponent, n	Intercept, b
Na.....	212.20	1.30	3.73
K.....	542.70	2.90	-.57
Mg.....	9.03	1.94	-.03
Ca.....	9.90	2.00	-.003
Al.....	.23	2.50	.010
1.....	5.65	2.08	.067
2.....	1.75	1.57	.087
3.....	.07	3.78	.001
4.....	130.58	1.53	-.104
5.....	47.84	1.81	-.084
6.....	19.93	1.72	.031

TABLE 3. - PEO required to dewater the ion-exchanged clays

PEO conc, wt pct	Method[1]	PEO dosage, g/kg clay solids				
		Na^+	K^+	Mg^{++}	Ca^{++}	Al^{+++}
0.25	Exp.	22.48	5.43	1.51	1.57	0.34
.25	Calc.	22.36	5.43	1.51	1.57	.34
.05	Exp.	6.76	3.08	.65	.73	.22
.05	Calc.	7.76	3.10	.64	.70	.22
.01	Exp.	4.87	1.77	.22	.25	.17
.01	Calc.	3.90	1.73	.23	.31	.17

[1]Exp. = experimental; Calc. = calculated.

TABLE 4. - Ionic radii of the exchanged ions

Ion	Charge (c)	Ionic radius (R), A	Hydrated radius (H_R), A	R/c	H_R/c
Na...	1	0.95	3.58	0.95	3.58
K....	1	1.33	[1]1.33	1.33	1.33
Mg...	2	.65	4.28	.325	2.14
Ca...	2	.99	4.12	.495	2.06
Al...	3	.50	4.75	.167	1.58

[1]According to Nightingale (6), the potassium ion (K^+) is unhydrated in solution; therefore, this entry represents the unhydrated radius of potassium.

Relationship Between n and the Hydrated Radii

Figure 3 is a plot of n for the various ion-exchange forms of montmorillonite versus the charge, c, divided by the hydrated radius, H_R. The points fall close to a straight line. Therefore, the value of n depends on the ratio of the hydrated radius to the charge of the exchange ion. This is an indication of interaction between the hydrated exchange ion of the montmorillonite and the ether dipole of PEO. This type of bonding has been called a hydrogen bridge through a water molecule (7).

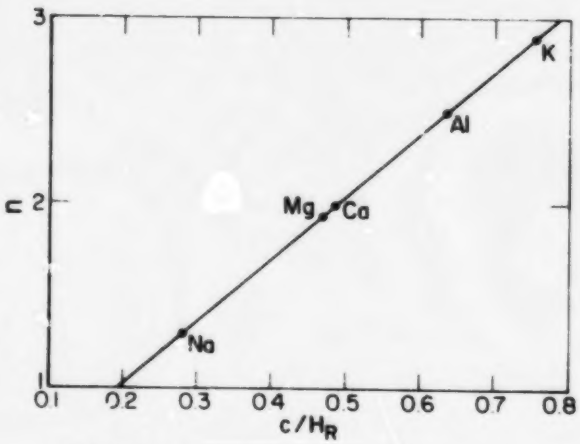

FIGURE 3. - Relation between n and c H_R.

Relationship Between k and the Unhydrated Ionic Radii

The value of the nth root of the constant k of equation 1 was found to be a function of R^2/c, where R is the ionic radius for all ions except sodium. For sodium, H_R is used. Figure 4 is a plot of $k^{1/n}$ taken from table 2 and R^2/c. The points lie on a straight line passing through the origin. A similar linear plot was also obtained with a constant k in a study of the dewaterability of ion-exchanged attapulgite clays (5). This lends confidence to the straight plot in figure 4. The need to use the hydrated radius for sodium apparently results from the nature of the system rather than from experimental error. This was indicated by repetition of the experiment producing similar results. Also the hydrated radius for sodium was required in the correlation of the dewatered percent data with A in a later section of this report. This correlation between k and unhydrated ionic radii indicates that more than bonding through a water bridge is involved in the interaction of PEO with montmorillonite.

BEST COPY AVAILABLE

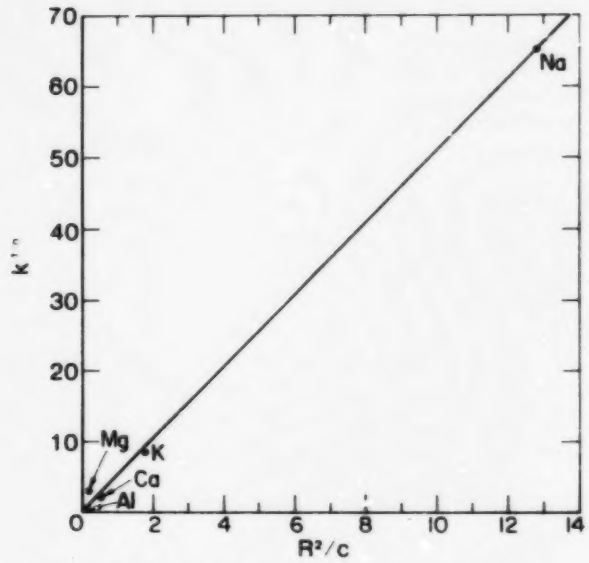

FIGURE 4. - Plot of $k^{1/n}$ versus R^2/c.

From the data an alternate relationship, in which A is proportional to R/c, can be derived. A proportionality constant, k_2, depends on the dilution of the polymer solution. Figure 5 contains plots of A versus R/c for each of the three polymer dilutions. The graphs of figure 5 can be represented by the equation

$$A = \frac{k_2 R}{c}. \qquad (2)$$

This relationship, established by figure 5, indicates that polymer concentration is an important factor in determining how PEO interacts with the exchange ion of the clay.

Relationship of the Solids Content to the Ionic Radii

The solids contents of the dewatered clays are given in table 5 for the different ion-exchanged clays. The measured solids contents were believed to have a large experimental error because they were influenced by the amount and vigor, of hand squeezing. In table 5 the calculated values were obtained by using a statistical technique called factor analysis (8). The purpose of factor analysis in this application is to remove part of the experimental error. The experimental solids contents are plotted versus the

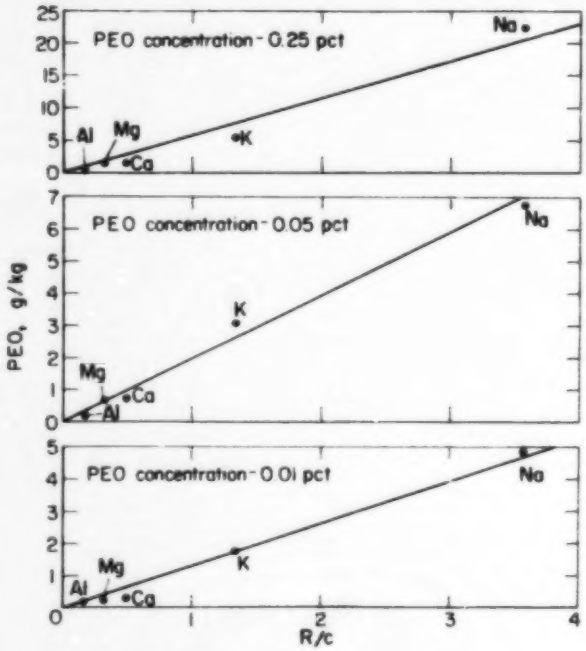

FIGURE 5. - Plots of A and R c.

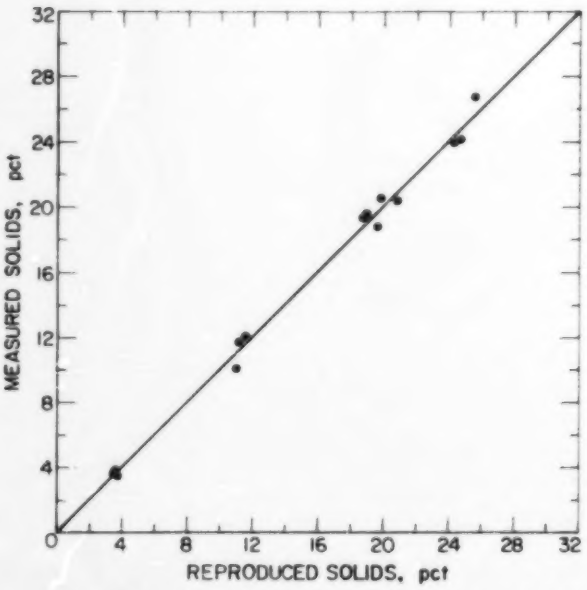

FIGURE 6. - Plot of observed percent solids data versus one-factor reproduced data.

calculated one-factor solids contents in figure 6. The points scatter around a straight line with a slope of 45°. This is a strong indication that the points are reproduced adequately by one-factor error analysis. A second factor would

BEST COPY AVAILABLE

TABLE 5. - Measured solids content and one-factor reproduced solids content

PEO conc, wt pct	Method[1]	Dewatered material, pct solids				
		Na	K	Mg	Ca	Al
0.25	Exp.	3.49	12.00	18.67	20.38	26.67
.25	Calc.	3.73	11.54	19.69	20.88	25.66
.05	Exp.	3.80	11.60	19.53	20.07	24.14
.05	Calc.	3.60	11.13	18.99	20.14	24.74
.01	Exp.	3.60	10.00	19.23	20.45	23.94
.01	Calc.	3.55	10.97	18.72	19.85	24.39

[1]Exp. = experimental; calc. = calculated.

cause the slope of the line in figure 1 to differ from 45°. Details of the application of this technique are provided by Malinowski (8).

To determine the relationship between the amount of polymer, A, required for dewatering and the solids content, A is plotted against the reciprocal of the one-factor reproduced solids content in figure 7. The data fall on three straight lines, one for each concentration, passing through the point 0.034 on the X axis. The data represented in figure 7 can be reproduced by the equation

$$A = k_3 (s-0.034), \qquad (3)$$

where s is the reciprocal of the solids content (1/pct solids), and k_3 is the slope of an individual line. Since A in equation 2 is proportional to R/c, and A in equation 3 is proportional to s, therefore s should be proportional to R/c. This is illustrated in figure 8

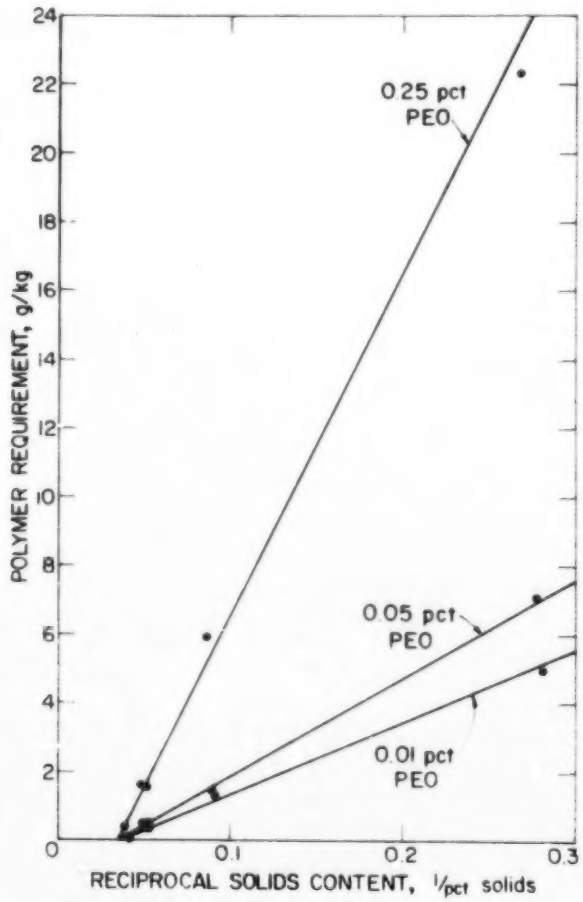

FIGURE 7. - Relation between A and percent solids for data reproduced from one-factor statistical analysis.

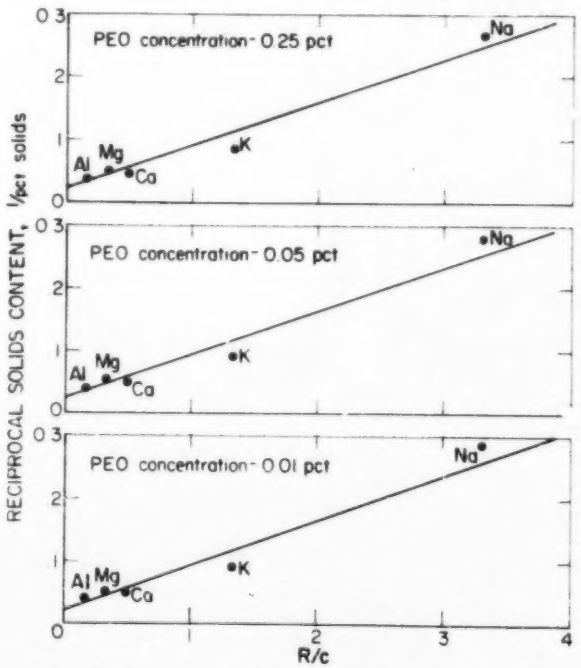

FIGURE 8. - Plots of reciprocal of percent solids versus R/c.

BEST COPY AVAILABLE

FIGURE 9. - Photomicrograph of Na-exchanged montmorillonite dewatered by PEO.

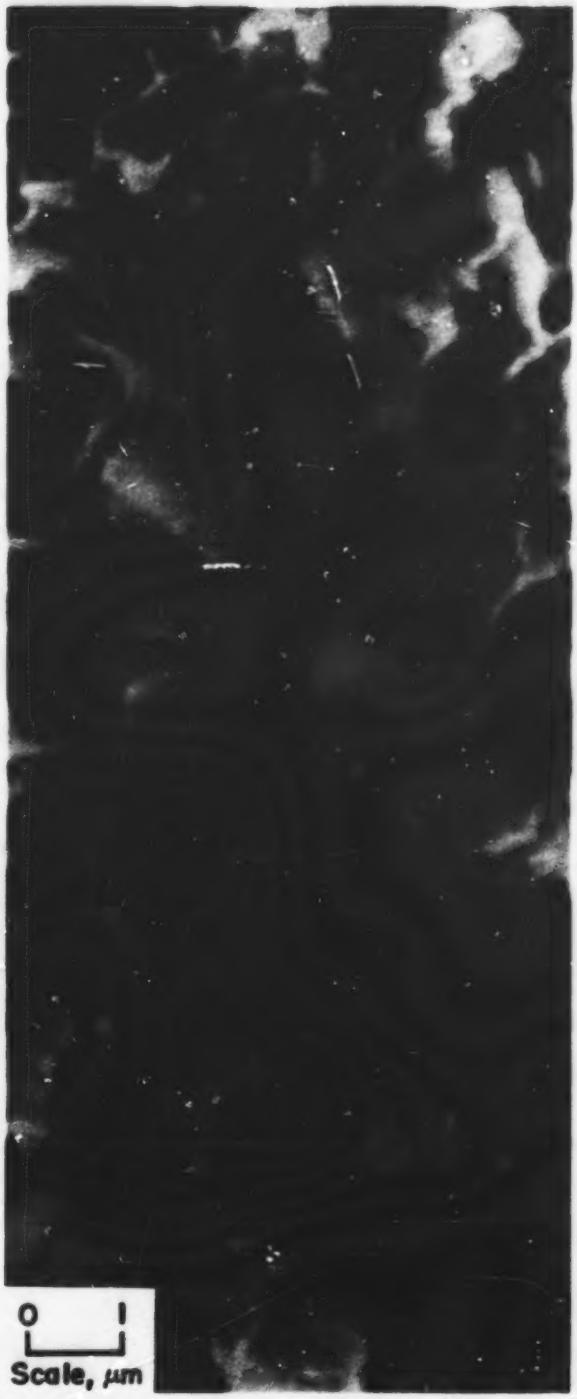

FIGURE 10. - Photomicrograph of Ba-exchanged montmorillonite dewatered by PEO.

BEST COPY AVAILABLE

with plots of s versus R/c for three concentrations of PEO. This relationship indicates that the solids content of the dewatered clay is dependent on the dosage and the exchange ion of the clay.

ELECTRON PHOTOMICROGRAPHS

Figure 9 is a scanning electron photomicrograph of an Na-exchanged clay dewatered by PEO. This open structure is due to strong edge-to-face interaction, which has been described as "card house floc" by Michaels and Bolger (9). This cellular structure due to internal mutual flocculation is responsible for the high water retention of the Na-exchanged clays and their low dewatered solids contents (10). Figure 10 is a scanning electron photomicrograph of a Ca-exchanged montmorillonite that had been dewatered with PEO. The individual montmorillonite platelets have been joined edge to edge and face to face to form extremely compact aggregates. A similar compact arrangement was observed in dewatered attapulgite (5). These photomicrographs are evidence that PEO adsorption can bond montmorillonite plates through both the plate faces and the edges. Similar behavior has been shown in viscometric studies in which vinyl acetate malic anhydride can bond montmorillonite platelets both face to face and edge to edge (11).

DISCUSSION AND CONCLUSIONS

The results of this study indicate the following relationships for montmorillonite dewatering with PEO:

1. The equation $A^n = kC + b$ describes the experimental results observed in this study.
2. The exponent, n, is determined by the charge and the hydrated ionic radius.
3. The term R^2/c determines the value of k.
4. $\frac{k_2 R}{c} = A = k_3 (s-0.034)$.

The PEO dewatering technique is a two-stage process (12). In the first stage, PEO is reacted with clay under the influence of shear provided by the stirrer. In the second stage, the resulting flocs are subjected to mechanical deformation on the static screen and rotary trommel. In laboratory experiments, hand squeezing simulates the mechanical deformation of the trommel. The established relations from this study suggest the following:

1. The exponent, n, involves the process of uncoiling of the random PEO coil under the influence of the exchange ion and shear (12).
2. The value of k is established in the second stage of the dewatering process where the initial open floc structure is being forced into an edge-to-edge and face-to-face interaction between the clay particles.
3. The solids content of the dewatered product is dependent on the amount of PEO used and the ion-exchange form of the clay.

The electron photomicrographs show a very open structure for the sodium montmorillonite even after dewatering. The Ca-exchanged montmorillonite shows very compact structures after dewatering with PEO. The dewatered solids content of the Na-exchanged clay increases only slightly over the initial solids content of the slurry. On the other hand, the dewatered solids content for Ca-exchanged clay increases to an average value of 20.3 pct. This suggests that the photomicrograph of the dewatered Na-exchanged clay represents an open structure typical of clays in low-density slurries and that the compact Ca-exchanged clay structure represents the condition of a highly dewatered clay.

The data indicate that dewatered solids content increases with values of R/c. This may be due to decreased strength of the gel, to increased strength of the PEO bonding to the surface ions, or to both.

The PEO dewatering technique from a mechanistic standpoint is a very complex system that will require further research to explain it in its entirety.

BEST COPY AVAILABLE

REFERENCES

1. Scheiner, B. J., A. G. Smelley, and D. R. Brooks. Large-Scale Dewatering of Phosphatic Clay Waste From Central Florida. BuMines RI 8611, 1982, 11 pp.

2. Brown, P. M., and B. J. Scheiner. Dewatering of Coal-Clay Waste Slurries From Preparation Plants. BuMines RI 8824, 1983, 8 pp.

3. Smelley, A. G., and I. L. Feld. Flocculation Dewatering of Florida Phosphatic Clay Wastes. BuMines RI 8349, 1979, 26 pp.

4. Stanley, D. A., P. M. Brown, and B. J. Scheiner. The Effect of Ion Exchange on the Dewatering of Phosphate Clay Waste With Polyethylene Oxide. Paper in Proceedings of Progress in the Dewatering of Fine Particles Conference. Univ. AL, Tuscaloosa, AL, 1981, 14 pp.

5. Stanley, D. A., and B. J. Scheiner. Mechanically Induced Dewatering of Ion Exchanged Attapulgite Flocculated by a High Molecular Weight Polymer. Colloids and Surfaces, v. 14, 1985, pp. 151-159.

6. Nightingale, E. R., Jr. Phenomenological Theory of Ion Solvation: Effective Radii of Hydrated Ions. J. Phys. Chem., v. 63, 1959, pp. 1381-1387.

7. Theng, B. K. G. Formation and Properties of Clay-Polymer Complexes. Elsevier N. Holland, 1979, 362 pp.

8. Malinowski, E. R. Factor Analysis in Chemistry. Wiley, 1980, 251 pp.

9. Michaels, A. S., and J. C. Bolger. Particle Interactions in Aqueous Kaolinite Dispersions. Ind. and Eng. Chem., Fundam., v. 3, 1964, pp. 14-20.

10. Van Olphen, H. Internal Mutual Flocculation in Clay Suspensions. J. Colloid Sci., v. 19, 1964, pp. 313-322.

11. Van Der Watt, H. V. H., and C. B. Bodman. Viscometric Constants of Suspensions of Clay Polymer Complexes. Paper in Proceedings of 9th National Conference on Clays and Clay Minerals. Pergamon, New York, v. 9, 1962, pp. 568-584.

12. Scheiner, B. J., A. G. Smelley, and D. A. Stanley. Dewatering of Mineral Waste With the Flocculant Polyethylene Oxide. BuMines B 681, 1985, 18 pp.

U.S. GOVERNMENT PRINTING OFFICE: 1988—605-017/40,032

INT.-BU.OF MINES,PGH.,PA. 28238

BEST COPY AVAILABLE